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SYMMETRY AND DESIGN IN MIXTURE EXPERIMENTS

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Two types of symmetry can arise when the proportions of mixture components are constrained by upper and lower bounds. These two types of symmetry are shown to be useful for blocking first-order designs, as well as for finding the centroid of the experimental region. Regions with both types of symmetry are used to develop response surface designs for mixtures. The uniform shell designs can be expressed as mixture designs with only three levels. The central composite design and designs based on the icosahedron and the dodecahedron are given for four-component mixture systems. A uniform shell design is applied to the development of an obscurant smoke.

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PREFACE

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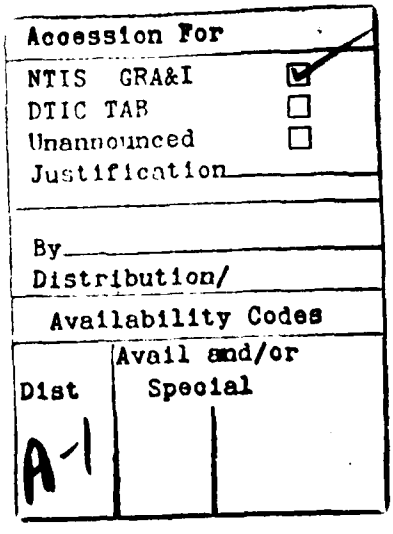

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SYMMETRY AND DESIGN IN MIXTURE EXPERIMENTS

1. INTRODUCTION

Many products, such as oils, cements, gasolines, and perfumes, are mixtures of components. The development of better products of these types involves experimentation with different formulations, or blends, of the components. In these experiments, the components are not usually allowed to vary over the full range of 0-100% but are subjected to upper and lower bound constraints for physical, chemical, or economic reasons. Under certain conditions, the upper and lower bound constraints create an experimental region with symmetry properties that are useful in finding the centroid of the region and in blocking first-order response surface designs.

Symmetric regions are also useful in deriving second-order response surface designs for mixture experiments. Kurotori[1] proposed that the simplex-lattice designs of Scheffe[2] be mapped into a constrained mixture region. There is no compelling reason to use a simplex-shaped design for a subregion of the mixture space; Kurotori's[1] proposal was based on ease of use. Thompson and Myers[3] proposed the use of rotatable response surface designs to explore a constrained mixture region. Although it seems natural to explore the region around the current product formulation by a rotatable design, the proposal of Thompson and Myers[3] has not been popular. Their method of mapping a response surface design for nonmixture variables to a constrained mixture region requires matrix manipulations. In contrast, Kurotori's[1] mapping of simplex-shaped designs to constrained mixture regions only requires a simple linear transformation. Response surface designs for mixture experiments may be derived by geometry directly from symmetric regions. The designs are then expressed in terms of component proportions, rather than as nonmixture variables, and can be mapped to a constrained region by a simple linear transformation.[1,4] In addition, the geometrically derived designs have a more natural orientation than designs obtained by the matrix method of Thompson and Myers.[3] For example, the geometrically derived designs generally have fewer levels of the component proportions than designs derived by matrix manipulation, and the geometrically derived designs treat all components equally; whereas, the matrix-derived designs usually do not.

Section 2 reviews the geometry of constrained mixture spaces, the use of pseudocomponents, and the blocking of mixture designs, which is a major use of symmetry in mixture experiments. Sections 3 and 4 each identify a type of symmetry and examine its usefulness in blocking mixture experiments. Section 5 presents several second-order designs for mixture experiments and Section 6 applies

a mixture design to the development of an obscurant smoke. The appendix shows that the three-level mixture designs described in this report are the uniform shell designs of Doehlert.[5]

2. BACKGROUND

2.1 *Geometry.*

The natural bounds on the component proportions $0 \leq x_i \leq 1$ for $i = 1,2,...,q$ define a hypercube in q-dimensional space. The mixture constraint plane $\sum_{i=1}^{q} x_i = 1$ intersects the hypercube to form a regular $(q-1)$-dimensional simplex. The simplex is actually formed by the intersection of the lower bounds $0 \leq x_i$ with the mixture constraint plane; the upper bounds $x_i \leq 1$ intersect the simplex only at its vertices.

Additional constraints of the form $0 \leq L_i \leq x_i \leq U_i \leq 1$ define a rectangular region in q-dimensional space. The mixture constraint plane intersects this rectangular region to form the experimental region, which is, therefore, a rectangular section. An alternative view, which is helpful in working with mixture experiments, is to define the experimental region as the intersection of two simplexes. One simplex is formed by the intersection of the lower bound constraints and the mixture constraint and is referred to as the L simplex. The other simplex, called the U simplex, is formed by the intersection of the upper bounds and the mixture constraint. The U simplex has an orientation opposite that of the L simplex (the directions of the vertices and faces are switched along the axes). The quantities

$$R_L = 1 - \sum_{i=1}^{q} L_i \tag{1}$$

and

$$R_U = \sum_{i=1}^{q} U_i - 1 \tag{2}$$

are the relative sizes of the L and U simplexes, respectively, to the simplex of unconstrained mixture components.

The constraints on the component proportions determine the size, shape, location, and orientation of the experimental region; this is too much information for the study of symmetry, which is based on shape only. It is possible to obtain a one-to-one correspondence between the constraints and the shape of the experimental region by transforming the component proportions to a new set of variables called pseudocomponents.

2.2 *Pseudocomponents.*

Pseudocomponents are defined as

$$z_i = (x_i - L_i)/R_L \text{ if } R_L \leq R_U \tag{3}$$

or

$$z_i = (U_i - x_i)/R_U \text{ if } R_U < R_L \tag{4}$$

Note that there are actually two pseudocomponent transformations, one based on the lower bound constraints, the other based on the upper bound constraints. Given that the upper and lower bounds are defined so that each component can attain both its upper and lower bounds (and this can always be done), pseudocomponents always have lower bounds of zero and upper bounds B_i given by

$$B_i = R_i / R_P \tag{5}$$

where $R_i = U_i - L_i$ is the range of the ith component and R_P is the minimum of R_L and R_U. The set of pseudocomponent upper bounds completely determines the shape of a mixture region constrained by upper and lower bounds.

An inverse pseudocomponent transformation

$$x_i = L_i + R_L \cdot z_i \tag{6}$$

or

$$x_i = U_i - R_U \cdot z_i \tag{7}$$

may be used to map a standard mixture design (expressed as z's) to the constrained region for an experiment (expressed as x's, the proportions of the components). A standard mixture design is a mixture design centered at $(1/q, 1/q, ..., 1/q)$, the centroid of the mixture space for q components. This definition includes the simplex-lattice and simplex-centroid designs of Scheffe,[2,6] the symmetric-simplex designs of Murty and Das,[7] and the designs discussed in this report.

2.3 *Blocking.*

Orthogonal blocking means the contrast representing the block effect is orthogonal to every term in the model. To develop the conditions for orthogonal blocking of a mixture experiment, consider a simple case: a design for three components divided into two blocks. Let the block contrast have a coefficient of -1 for the first block and a coefficient of 1 for the second block. Let a_1, b_1, and c_1 be the sums of x_1, x_2, and x_3, respectively, in the first block, and a_2, b_2, and c_2 be the sums of x_1, x_2, and x_3 in the second block. The requirement for the first-order

terms to be orthogonal to the block contrast is that $a_1 = a_2$, $b_1 = b_2$, and $c_1 = c_2$. Because x_1, x_2, and x_3 are proportions, $a_1 + b_1 + c_1$ is equal to the number of observations in the first block, and $a_2 + b_2 + c_2$ is equal to the number of observations in the second block. Therefore the blocks must be of equal sizes if the simple coding, -1 and 1, is used for the block contrast.

Second-degree canonical polynomials contain cross product terms of the form $x_i x_j$. For these second-order terms to be orthogonal to the block contrast, the sum of $x_i x_j$ in the first block must be equal to the sum of $x_i x_j$ in the second block. These blocking requirements are readily generalized to more than two blocks: the sum of x_i (and $x_i x_j$ for second-order models) must be the same in each block. This allows simple orthogonal contrasts, such as, for three blocks, -1 0 1 and 1 -2 1, to be used for the block effects in the analysis.

Blocking schemes with unequal block sizes can be developed. For two blocks of sizes n_1 and n_2, the coefficients for the block contrast should be proportional to $-1/n_1$ and $1/n_2$. The blocking requirement for the first-order terms then becomes $n_2 \cdot a_1 = n_1 \cdot a_2$, $n_2 \cdot b_1 = n_1 \cdot b_2$, etc.; a similar requirement applies to the second-order terms.

3. TWIN SYMMETRY

A constrained mixture region will have a type of symmetry when the L and U simplexes are the same size. The mixture region for $0.2 \leq X_1 \leq 0.7$, $0.05 \leq X_2 \leq 0.65$, and $0.1 \leq X_3 \leq 0.3$, which has $R_L = R_U$, is presented in Figure 1. If one looks at Figure 1 upside down, the experimental region appears exactly the same as it does right side up. This is no coincidence; inverting Figure 1 interchanges the L and U simplexes, but, as the L and U simplexes are the same size, this produces the same experimental region. Every point in the experimental region has a twin that is the reflection of the point through the centroid. To find the twin of a point **x**, transform **x** to **z** by one pseudocomponent transformation, then transform **z** back to components by the inverse of the *other* pseudocomponent transformation. Because $R_L = R_U$, this calculation of the twin **t** of a point **x** reduces to $t_i = L_i + U_i - x_i$ for $i = 1,2,3,...,q$. As a mnemonic for the existence of pairs of twins in the experimental region, I call this type of symmetry *twin symmetry*. Twin symmetry has consequences for finding (and defining) the centroid of the experimental region and for blocking first-order designs.

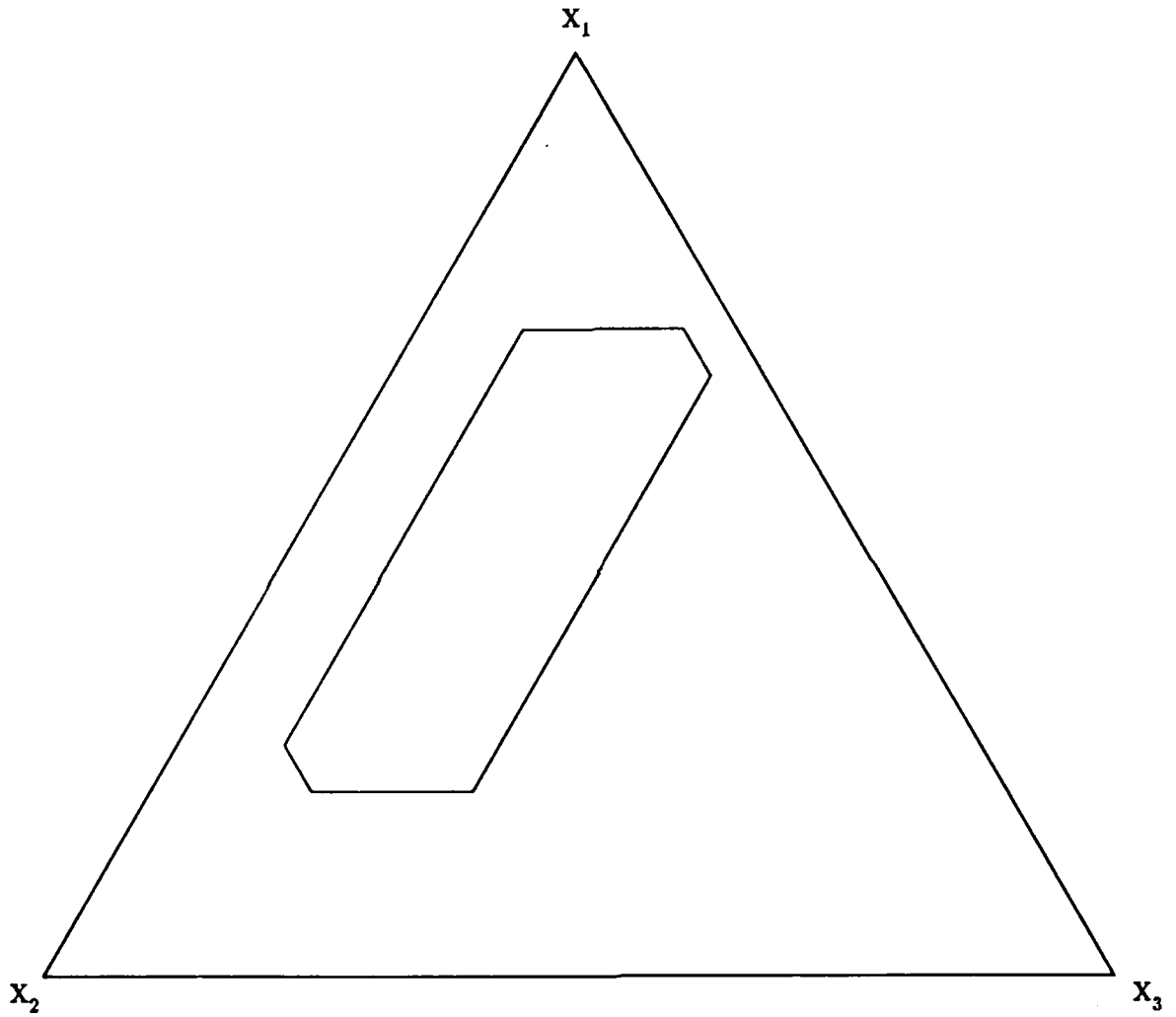

Figure 1. Twin Symmetry

Piepel[8] noted that averaging the vertices of a constrained mixture region does not necessarily yield the classical center-of-mass (COM) centroid. Thus, he viewed the average vertices (AV) centroid as an approximation of the COM centroid. Piepel[9] suggested a new technique for quickly estimating a centroid. His range normalized midrange (RNM) formula for a centroid is:

$$c_i = M_i - [R_i(\sum_{j=1}^{q} M_j - 1)/(\sum_{j=1}^{q} R_j)], \tag{8}$$

where $M_i = (L_i + U_i)/2$ is the midrange of the ith component. Piepel[9] noted that all three centroids (COM, AV, and RNM) are the same if the sum of the midranges is exactly one. This condition (sum of midranges equals one) is algebraically equivalent to $R_L = R_U$. Thus, whenever an experimental region has twin symmetry, its centroid is uniquely defined; further, the centroid is given by the component midranges (it is easily seen that the correction term in the RNM formula is zero when the sum of the midranges is one). Of no less importance is that any point in the experimental region and its twin average to the centroid. Pairs of twin points are, therefore, blocks with respect to first-order mixture designs.

3.1 *Example of Twin Symmetry.*

Snee and Marquardt[10] discuss a gasoline blending study in which the five components have bounds $0 \le x_1 \le 0.1$, $0 \le x_2 \le 0.1$, $0.05 \le x_3 \le 0.15$, $0.2 \le x_4 \le 0.4$, and $0.4 \le x_5 \le 0.6$, so that $R_L = R_U = 0.35$. The experimental region has 28 vertices; but, Snee and Marquardt[10] selected 16 vertices for use as a first-order design. The 16 vertices are 8 pairs of twins, or, for the first-order model, 8 blocks of size 2. The eight blocks could, for example, be assigned to the eight points of a 2^3 factorial design for three process variables. Then all seven effects of the 2^3 design in the process variables could be estimated orthogonally to the five mixture terms. The proposed design, with Snee and Marquardt's[10] numbering of the vertices and the levels of the process variables (w_1, w_2, w_3) coded as -1 and 1, is given in Table 1. With only 4 degrees of freedom for error, and no process variable times mixture component terms in the model, this design may be considered a screening design. Another block consisting of a replicated centroid point (centroid for both mixture and process variables) could be added to obtain another degree of freedom for error and 1 degree of freedom for curvature.

Table 1. Blocking by Twin Symmetry

Row	Block	Vertex	x_1	x_2	x_3	x_4	x_5	w_1	w_2	w_3
1	1	1	0.10	0.10	0.05	0.20	0.55	−1	−1	−1
2	1	8	0.00	0.00	0.15	0.40	0.45	−1	−1	−1
3	2	2	0.10	0.00	0.15	0.20	0.55	1	−1	−1
4	2	7	0.00	0.10	0.05	0.40	0.45	1	−1	−1
5	3	3	0.00	0.10	0.15	0.20	0.55	−1	1	−1
6	3	6	0.10	0.00	0.05	0.40	0.45	−1	1	−1
7	4	4	0.10	0.10	0.15	0.20	0.45	1	1	−1
8	4	5	0.00	0.00	0.05	0.40	0.55	1	1	−1
9	5	9	0.00	0.00	0.05	0.35	0.60	−1	−1	1
10	5	10	0.10	0.10	0.15	0.25	0.40	−1	−1	1
11	6	11	0.10	0.00	0.05	0.25	0.60	1	−1	1
12	6	26	0.00	0.10	0.15	0.35	0.40	1	−1	1
13	7	14	0.00	0.10	0.05	0.25	0.60	−1	1	1
14	7	23	0.10	0.00	0.15	0.35	0.40	−1	1	1
15	8	17	0.00	0.00	0.15	0.25	0.60	1	1	1
16	8	20	0.10	0.10	0.05	0.35	0.40	1	1	1

3.2 *Interpretation as Rectangular Sections.*

Often an experimenter defines the region of interest by adding and subtracting a half-range, h_i, to the level of the ith component in the current formulation. This defines a rectangular region in q-dimensional space whose centroid lies on the mixture plane. If c_i is the level of the ith component in the current formulation, then defining $L_i = c_i - h_i$ and $U_i = c_i + h_i$ leads immediately to $R_L = R_U$, which is the definition of twin symmetry. Thus, twin symmetry implies that the experimental region is a *central* section of a rectangular region. Experimenters often generate regions of interest with twin symmetry by defining the experimental region in terms of a centroid and a set of half-ranges. Conversely, all mixture regions with twin symmetry can be described by a centroid and a set of half-ranges.

3.3 *A Special Case: Parallelotope Regions.*

Another common procedure for specifying a region of interest in mixture experiments is to define the experimental region by a 2-level factorial design in the proportions of $q-1$ components. The qth component is adjusted to make the component proportions sum to one; therefore $L_q = 1 - \sum_{i=1}^{q-1} U_i$ and $U_q = 1 - \sum_{i=1}^{q-1} L_i$.

The region so defined is a parallelotope (the generalization of parallelogram, parallelepiped, ...). Parallelotope regions (which have the condition on L_q and U_q) are a subset of regions with twin symmetry (which have the sum of midranges equal to 1). Although parallelotope regions have twin symmetry, designs for them are most easily obtained by their similarity to cuboidal regions. Saxena and Nigam[11] discuss a five component lubricating oil study in which the experimental region is a parallelotope. By analogy to a composite design for a 4-dimensional cube, the 16 vertices and 8 face centroids are an excellent second-order design for the parallelotope region. (The region does not have 32 faces, or 3-dimensional boundaries, as Saxena and Nigam[11] state, although it does have 32 edges.)

4. RADIAL SYMMETRY

There is another condition under which the three centroids (COM, AV, and RNM) are the same. Consider the constrained mixture region $0.1 \leq x_1 \leq 0.6$, $0.2 \leq x_2 \leq 0.7$, and $0.1 \leq x_3 \leq 0.6$. The midranges sum to 1.15, $R_L = 0.6$ and $R_U = 0.9$, but the centroid is $x_1 = 0.3$, $x_2 = 0.4$, and $x_3 = 0.3$ by any of the three methods. The component ranges are all equal for this example, and Figure 2 illustrates how equal component ranges affect the experimental region: the experimental region is a simplex (the L simplex here) whose vertices have been truncated at the same distance from the centroid. The experimental region shows a type of symmetry found in nature (e.g., starfish and daisies) and called *radial symmetry* (e.g., see Villee,[12] page 78). Because every vertex of the L simplex has been truncated in the same manner, the centroid of the L simplex is also the centroid of the experimental region. This gives an easy method of calculating the centroid of the experimental region when the component ranges are equal: transform $\mathbf{z} = (1/q)\mathbf{1}$ by an inverse pseudocomponent transformation. The inverse of either pseudocomponent transformation may be used here: radial symmetry is due to the L and U simplexes having the same centroid.

Radial symmetry, like twin symmetry, creates related points in the experimental region. In a radially symmetric region, there are q symmetrically placed points that average to the centroid of the region. To find the $q - 1$ points symmetrically placed to a point $\mathbf{x}$, transform the point $\mathbf{x}$ to pseudocomponents $\mathbf{z}$, then *cyclically* permute the levels of $\mathbf{z}$. For example, if $\mathbf{z}' = (a, b, c)$, then the permutations are (b, c, a) and (c, a, b). Finally, transform each permutation back to components. The cyclical permutation *must* be done in pseudocomponent units, but the q radially symmetric points will average to the centroid when expressed in component units.

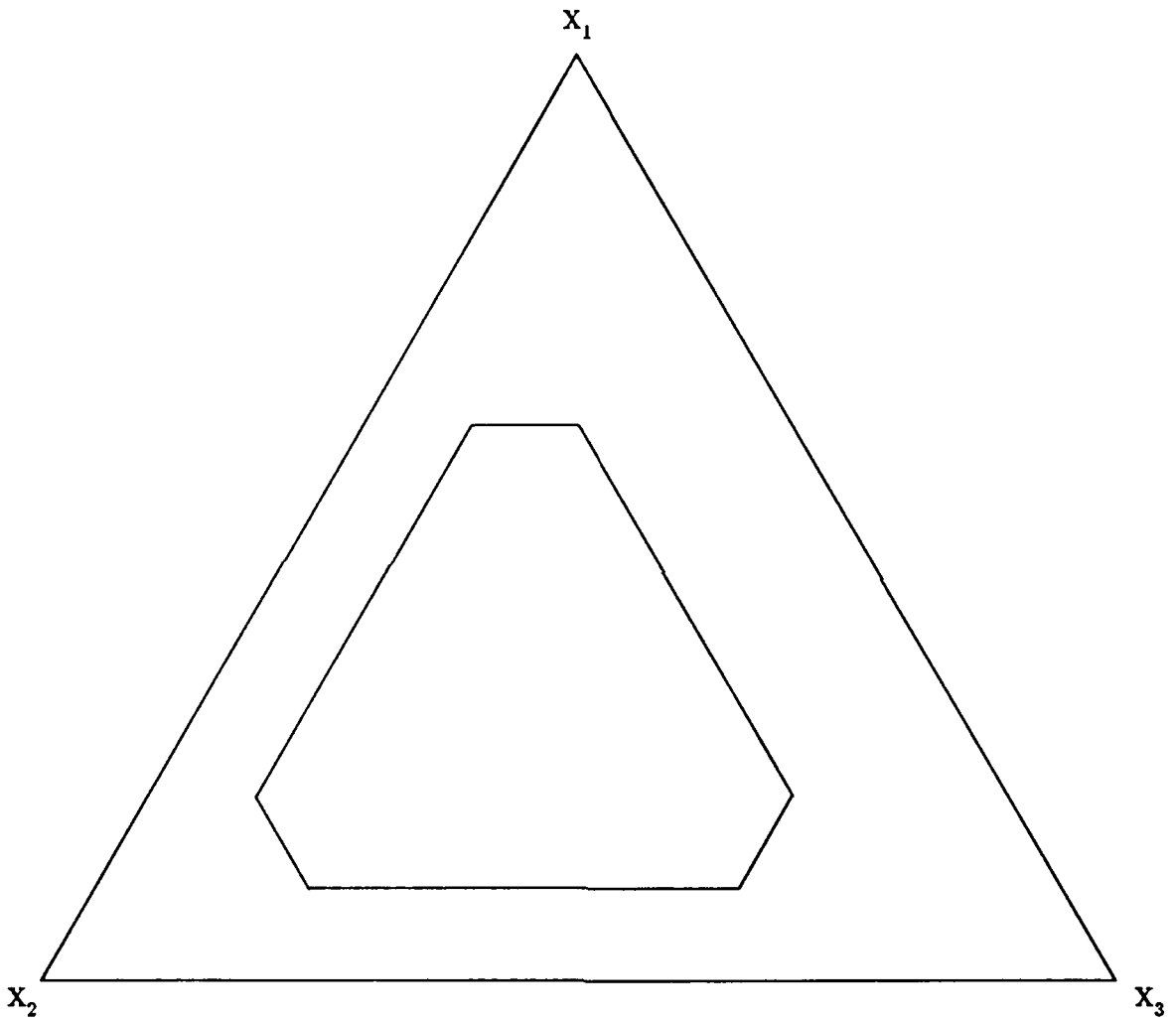

Figure 2. Radial Symmetry

Radial symmetry also provides opportunities for blocking first-order designs. Table 2 presents a first-order design for four components with lower bounds 0, 0.1, 0.2, and 0.3 and upper bounds 0.24, 0.34, 0.44, and 0.54. The design is the 12 vertices of the constrained region. The blocks are easily identified from the cyclic permutations of the pseudocomponent values (z_i) given in Table 2.

Table 2. Blocking by Radial Symmetry

Vertex	z_1	z_2	z_3	z_4	Block	x_1	x_2	x_3	x_4
1	0.6	0.4	0.0	0.0	1	0.24	0.26	0.20	0.30
2	0.0	0.6	0.4	0.0	1	0.00	0.34	0.36	0.30
3	0.0	0.0	0.6	0.4	1	0.00	0.10	0.44	0.46
4	0.4	0.0	0.0	0.6	1	0.16	0.10	0.20	0.54
5	0.6	0.0	0.4	0.0	2	0.24	0.10	0.36	0.30
6	0.0	0.6	0.0	0.4	2	0.00	0.34	0.20	0.46
7	0.4	0.0	0.6	0.0	2	0.16	0.10	0.44	0.30
8	0.0	0.4	0.0	0.6	2	0.00	0.26	0.20	0.54
9	0.6	0.0	0.0	0.4	3	0.24	0.10	0.20	0.46
10	0.4	0.6	0.0	0.0	3	0.16	0.34	0.20	0.30
11	0.0	0.4	0.6	0.0	3	0.00	0.26	0.44	0.30
12	0.0	0.0	0.4	0.6	3	0.00	0.10	0.36	0.54

When expressed in pseudocomponents, radially symmetric regions have lower bounds of zero and a common upper bound, B. Hence all radially symmetric regions can be indexed by only two parameters: q and B. A region can have both radial and twin symmetries; such regions have $B = 2/q$. The study of regions with both twin and radial symmetries led to the development of the second-order designs described in this report.

Interpretation as Cuboidal Sections.

The use of equal component ranges creates a hypercube, rather than a rectangular region, in q-dimensional space. Thus, a radially symmetric region is a cuboidal rather than a rectangular section. A mixture region with both twin and radial symmetries is a *central* section of a q-dimensional cube.

5. SECOND-ORDER DESIGNS

5.1 *Mixture Designs.*

A design for a mixture experiment is an N by q matrix specifying the proportions of the q components for the N blends to be used in the experiment. A mixture design can be viewed as N points in $(q-1)$-dimensional space. As such, it does not matter if the design is described in terms of either q proportions, or $q-1$ functionally independent variables. In mixture experiments, the polynomial models commonly used in response surface methodology are usually reparameterized from $q-1$ variables to q proportions by using Scheffe's[2] canonical polynomials. The predictions of a polynomial model and the variances of those predictions are not affected by the reparameterization. Therefore, design criteria based on prediction variance, such as rotatability and G-efficiency (see Box and Draper[13] for a discussion of these), are applicable when response surface designs are used for mixture models. Other design criteria and features may not be applicable when response surface designs are used for mixture experiments.

Murty and Das[7] introduced the concept of symmetric-simplex designs for estimating the coefficients of Scheffe's[2] second-degree mixture polynomials. A mixture design is a symmetric-simplex design if, for each point in the design, all other points obtained by permuting the levels of the components are also in the design. Thus, a symmetric-simplex design can be indicated by a few typical points; all other points in the design can be obtained by permuting the levels of the typical points. For example, the simplex-centroid design[6] for $q = 3$ can be given by three typical points: (1, 0, 0), (1/2, 1/2, 0), and (1/3, 1/3, 1/3).

A natural method to develop standard mixture designs with symmetry properties is to construct designs from mixture regions that have both twin and radial symmetries; these regions have lower bounds of zero and upper bounds of $2/q$.

5.2 *Hexagon Design.*

For three-component mixtures, the region bounded by an upper bound of 2/3 on each component is a regular hexagon. The six vertices of the hexagon plus the centroid (preferably replicated) form a rotatable second-order design.[14] The hexagon design is a member of the class of uniform shell designs[5] and is also a symmetric-simplex design with two typical points: (2/3, 0, 1/3) and (1/3, 1/3, 1/3). Note that this is a three-level design. It may be desirable to check for lack of fit by

using check points. As shown in Figure 3, the regular hexagon can be divided into six equilateral triangles that have a common apex at the center of the hexagon. The centroids of the six equilateral triangles are a natural set of check points; each check point is equidistant from the centroid and two vertices of the hexagon. The design, which can be blocked, is given in Table 3. The six check points can be divided into two sets of three. Either set may be put in block 1, and the other set in block 2. For a discussion of the selection and use of check points, see Shelton, Khuri, and Cornell.[15]

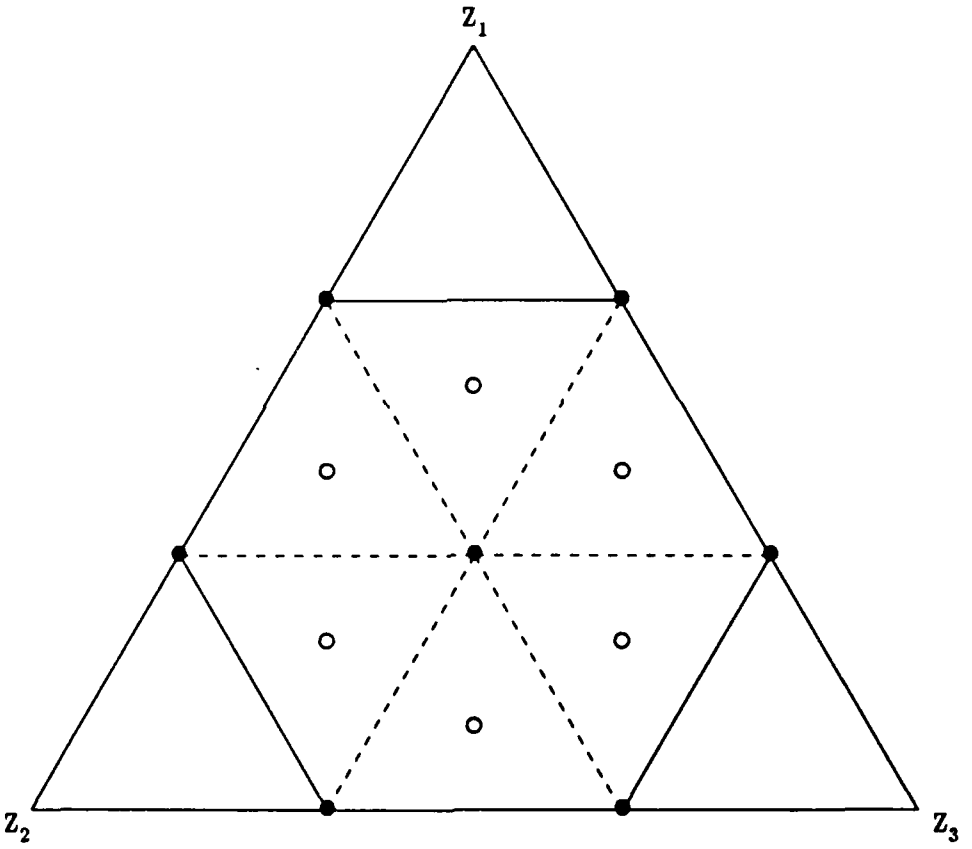

Figure 3. Hexagon Design (•) and Check Points (circles)

Table 3. Hexagon Design

Point	z_1	z_2	z_3	Block
1	2/3	0	1/3	1
2	1/3	2/3	0	1
3	0	1/3	2/3	1
4	1/3	1/3	1/3	1
5	1/3	1/3	1/3	1
6	2/3	1/3	0	2
7	0	2/3	1/3	2
8	1/3	0	2/3	2
9	1/3	1/3	1/3	2
10	1/3	1/3	1/3	2
11	5/9	2/9	2/9	1
12	2/9	5/9	2/9	1
13	2/9	2/9	5/9	1
14	1/9	4/9	4/9	2
15	4/9	1/9	4/9	2
16	4/9	4/9	1/9	2

Points 11-16 are optional check points.

5.3 *Composite Designs.*

For mixtures of four components, the region with both twin and radial symmetries is obtained by placing an upper bound of 1/2 on each component; these constraints reduce the experimental region to a regular octahedron (Figure 4). The octahedron has 6 vertices and 8 faces: the 6 vertices define 3 orthogonal axes, and the centroids of the 8 faces determine the axes of a four-component mixture system. The octahedron therefore links mixture and nonmixture representations of 3-dimensional experimental designs. It should not be surprising, then, to find that the commonly used response surface designs for three (independently adjustable) factors can be expressed naturally as designs for four-component mixture experiments. As the second-order polynomial has 10 parameters, the 6 vertices of the octahedron are clearly inadequate as a second-order design. The centroids of the 8 faces can be added to the 6 vertices and the centroid to obtain the 3-dimensional central composite design. The central composite design is usually obtained from the vertices and face centroids of a cube, but the cube and the octahedron are *dual* to each other; either can be inscribed inside the other with the vertices of the inscribed polyhedron at the face centroids of the other polyhedron. The only difference between the octahedral composite design and the cuboidal composite design is that the relative distances of the 6- and 8-point groups from the

centroid are interchanged. [The cuboidal composite design for functionally independent variables has 6 axial or star points at a radius of 1 and 8 factorial points at a radius of $3^{1/2}$; the octahedral composite design for mixtures has 8 face centroids at a radius of $12^{-1/2}$ and 6 vertices at a radius of $4^{-1/2}$. Note the ratio $(4/12)^{-1/2} = 3^{1/2}$.] The composite design for mixtures can be made spherical by shrinking the vertices of the octahedron back to the radius of the face centroids. The design is given in Table 4 in symmetric-simplex form.

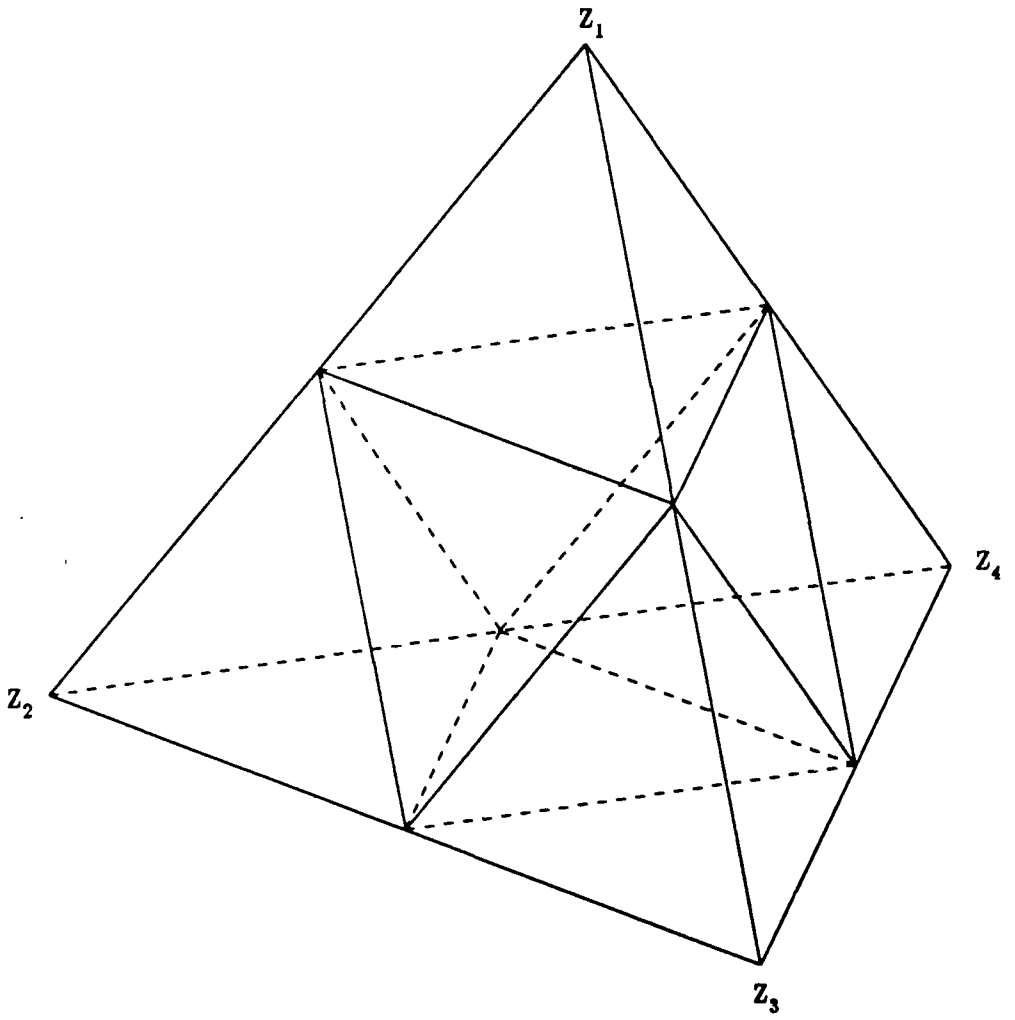

Figure 4. Tetrahedron Truncated to Octahedron

Table 4. Central Composite Designs

Point	z_1	z_2	z_3	z_4	Two Blocks	Three Blocks	Nearly Rotatable
1	1/2	1/6	1/6	1/6	1	1	1
2	1/6	1/2	1/6	1/6	1	1	1
3	1/6	1/6	1/2	1/6	1	1	1
4	1/6	1/6	1/6	1/2	1	1	1
5	0	1/3	1/3	1/3	1	2	1
6	1/3	0	1/3	1/3	1	2	1
7	1/3	1/3	0	1/3	1	2	1
8	1/3	1/3	1/3	0	1	2	1
9	a	a	b	b	2	3	2
10	a	b	a	b	2	3	2
11	a	b	b	a	2	3	2
12	b	a	a	b	2	3	2
13	b	a	b	a	2	3	2
14	b	b	a	a	2	3	2
15	1/4	1/4	1/4	1/4	2	1	1
16	1/4	1/4	1/4	1/4	2	1	1
17	1/4	1/4	1/4	1/4	-	2	2
18	1/4	1/4	1/4	1/4	-	2	-

Design	a	b
Octahedral	$0 = 0.0000$	$1/2 = 0.5000$
Spherical	$1/4 - (1/48)^{1/2} = 0.1057$	$1/4 + (1/48)^{1/2} = 0.3943$
Rotatable	$1/4 - 2592^{-1/4} = 0.1099$	$1/4 + 2592^{-1/4} = 0.3901$
Two Blocks	$1/12 = 0.0833$	$5/12 = 0.4167$
Three Blocks	$1/4 - (1/72)^{1/2} = 0.1321$	$1/4 + (1/72)^{1/2} = 0.3679$
Nearly Rotatable	$1/4 - (7/360)^{1/2} = 0.1106$	$1/4 + (7/360)^{1/2} = 0.3894$

This composite design for mixtures can be blocked into two blocks of eight, three blocks of six, or into blocks of different sizes. For 2 blocks of 8, 1 block consists of the 8 face centroids and the other block consists of 2 center points plus the 6 vertices moved to a radius of $9^{-1/2}$. This blocking requires use of the values $a = 1/12$ and $b = 5/12$, as given in Table 4. For 3 blocks of 6, the values $a = 1/4 - (1/72)^{1/2}$ and $b = 1/4 + (1/72)^{1/2}$ are required. The 3 blocks are (1) the upper face centroids plus 2 center points, (2) the lower face centroids plus 2 center points, and (3) the 6 vertices shrunk back to a radius of $18^{-1/2}$. For the blocking with unequal block sizes, the first block consists of the 8 face centroids plus 2 center points, and the second block consists of the 6 vertices shrunk back to a radius of $(7/90)^{1/2}$ plus 1 center point. This is a common method of blocking a composite design; the number of center points in each block is chosen to make the blocked design as rotatable as possible. For this nearly rotatable blocking, use

$a = 1/4 - (7/360)^{1/2} \approx 0.1106$ and $b = 1/4 + (7/360)^{1/2} \approx 0.3894$. With blocks of sizes 10 and 7, the coefficients for the block contrast must be proportional to $-1/10$ and $1/7$ for the first and second blocks, respectively; -7 and 10 are convenient.

5.4 *Cuboctahedron Design.*

The edge centroids and overall centroid of the octahedron form a second-order design. The 12 edge midpoints of the octahedron are the same points as the edge midpoints of a cube; hence, this gives a well known design.[5,16,17] The 12 points are equally distant from the centroid, and the design is considered a design for a spherical region. The radius of this sphere is $8^{-1/2}$, which is larger than the radius of the spherical composite design of Table 4, even though both designs vary the components over the same range. The design comparisons made by Lucas[18] are based on scaling the designs to have the same radius and are not necessarily applicable if the designs are scaled to have the same component ranges. The 12 design points on the sphere can be viewed as forming a convex polyhedron, known as a cuboctahedron (cube + octahedron), that has 14 faces: 6 squares and 8 equilateral triangles. Each of the eight triangular faces of the cuboctahedron, along with the centroid of the cuboctahedron, forms a regular simplex. The centroids of these eight simplexes may be used as check points; this is analogous to the development of check points for the hexagon design. The cuboctahedron design is not rotatable; the prediction variance is greater at points on the design radius intersected by lines from the centroid through the centers of the square faces than at other points on the sphere. The cuboctahedron design is given in Table 5 along with the icosahedron design, which is discussed in the next paragraph. Like the hexagon design, the cuboctahedron design is a symmetric-simplex design and a member of the class of uniform shell designs.[5] Box and Behnken[17] recommend three center points for this design.

5.5 *Icosahedron Design.*

An alternative to the cuboctahedron, or uniform shell, design is the icosahedron design. The icosahedron is the regular polyhedron with 20 faces and 12 vertices. The 12 vertices plus center points form a rotatable second-order design.[14] Toth[19] gives a derivation of the vertices of the icosahedron from an octahedron: thus, the points of the icosahedron design for a mixture experiment are readily determined from the octahedral region. The icosahedron design is not a symmetric-simplex design because only half of the permutations of (0.5, 0, 0.309, 0.191) are included in the design. The structure of the icosahedron design is similar

Table 5. Cuboctahedron and Icosahedron Designs

Point	z_1	z_2	z_3	z_4
1	1/2	0	a	b
2	1/2	b	0	a
3	1/2	a	b	0
4	0	1/2	b	a
5	a	1/2	0	b
6	b	1/2	a	0
7	0	a	1/2	b
8	b	0	1/2	a
9	a	b	1/2	0
10	0	b	a	1/2
11	a	0	b	1/2
12	b	a	0	1/2
13	1/4	1/4	1/4	1/4
14	1/4	1/4	1/4	1/4
15	1/4	1/4	1/4	1/4
16	7/16	3/16	3/16	3/16
17	3/16	7/16	3/16	3/16
18	3/16	3/16	7/16	3/16
19	3/16	3/16	3/16	7/16
20	1/16	5/16	5/16	5/16
21	5/16	1/16	5/16	5/16
22	5/16	5/16	1/16	5/16
23	5/16	5/16	5/16	1/16

Design	a	b
Cuboctahedron	$1/4 = 0.2500$	$1/4 = 0.2500$
Icosahedron	$1/(5^{1/2} + 1) = 0.3090$	$1/(5^{1/2} + 3) = 0.1910$

Points 16-23 are optional check points.

to the cuboctahedron, or uniform shell, design because the design points on the sphere for both designs lie on the edges of an octahedron. The uniform shell design uses the midpoints of the edges; whereas, the vertices of the icosahedron divide the edges into long and short segments [the ratio of the long segment to the short segment is $(5^{1/2} + 1)/2 = 1.618$, the *golden ratio*]. The permutations of (0.5, 0, 0.309, 0.191) not included in Table 5 form an equivalent icosahedron design obtained by switching the direction of the long and short segments along the edges of the octahedron. Proper randomization includes selecting one of the two equivalent icosahedron designs at random. The alternate form of the icosahedron design can be obtained by interchanging the values of a and b in Table 5. The check points listed in Table 5 may be used with the icosahedron design as well as with the uniform shell design.

5.6 *Dodecahedron Design.*

The dual of the icosahedron is the dodecahedron, which has 12 faces and 20 vertices. The 20 vertices plus center points form the dodecahedron design, which is a rotatable design.[14] If five center points are used, the dodecahedron design can be blocked into five blocks of five points each. The design is given in Table 6. Like the icosahedron design from which it was derived, the dodecahedron design is not a symmetric-simplex design, and there is an alternate form that can be obtained by interchanging the values of a and b in Table 6. There are two equivalent blocking schemes for the dodecahedron design. The first assigns the permutations of (0, 1/3, 1/3, 1/3) to a single block and the permutations of (1/2, 1/6, 1/6, 1/6) to different blocks; the other blocking scheme reverses this assignment. The alternate blocking scheme is also given in Table 6. The design radius of the dodecahedron design is $12^{-1/2}$, the same as that of the spherical composite design.

5.7 *Uniform Shell Designs.*

The uniform shell designs generalize to more than four components; they consist of shell points, given by all permutations of $(2/q, 0, 1/q, ..., 1/q)$, and the centroid $(1/q, \ldots, 1/q)$. A set of q check points for these designs is given by the permutations of $[(2q - 1)/q^2, (q - 1)/q^2, \ldots, (q - 1)/q^2]$. An alternate set of q check points is given by the permutations of $[1/q^2, (q + 1)/q^2, \ldots, (q + 1)/q^2]$. The design radius of uniform shell designs for mixtures is $2^{1/2}/q$, which is larger than $[1/q(q - 1)]^{1/2}$, the radius of a sphere inscribed inside the mixture simplex. Of course, the design points lie inside the mixture space, but a part of the sphere of the design radius extends beyond the faces of the simplex.

Table 6. Dodecahedron Design

Point	z_1	z_2	z_3	z_4	Blocking	Alternative
1	1/6	1/3	a	b	1	2
2	1/6	b	1/3	a	1	3
3	1/6	a	b	1/3	1	4
4	1/2	1/6	1/6	1/6	1	5
5	1/4	1/4	1/4	1/4	1	1
6	1/3	1/6	b	a	2	1
7	a	1/6	1/3	b	2	3
8	b	1/6	a	1/3	2	4
9	1/6	1/2	1/6	1/6	2	5
10	1/4	1/4	1/4	1/4	2	2
11	1/3	a	1/6	b	3	1
12	b	1/3	1/6	a	3	2
13	a	b	1/6	1/3	3	4
14	1/6	1/6	1/2	1/6	3	5
15	1/4	1/4	1/4	1/4	3	3
16	1/3	b	a	1/6	4	1
17	a	1/3	b	1/6	4	2
18	b	a	1/3	1/6	4	3
19	1/6	1/6	1/6	1/2	4	5
20	1/4	1/4	1/4	1/4	4	4
21	0	1/3	1/3	1/3	5	1
22	1/3	0	1/3	1/3	5	2
23	1/3	1/3	0	1/3	5	3
24	1/3	1/3	1/3	0	5	4
25	1/4	1/4	1/4	1/4	5	5

$$a = 1/3(5^{1/2} + 3) \approx 0.0637;$$
$$b = (5^{1/2} + 2)/3(5^{1/2} + 1) \approx 0.4363.$$

6. EXAMPLE

Obscurant smokes are used to hide military targets from the enemy's view. In modern warfare, the smokescreen must not only block the enemy's view but must also defeat devices that use infrared (IR) and radar frequencies. To block transmission of electromagnetic waves at the visible, IR, and radar frequencies, an obscurant smoke may be made from three components — powder, flake, and fiber — that block transmission at the visible, IR, and radar frequencies. From the known properties of the individual components, it can be estimated that a mixture of 20% powder, 30% flake, and 50% fiber would yield acceptable blockage in all three frequency bands. There is, however, good reason to suspect that this straightforward calculation is not correct. The flakes act as a lubricant that prevents the fibers from entangling as they otherwise would, and the powder particles tend to coat the surface of the much larger flake and fiber particles. This coating phenomenon changes the interaction of the particles with electromagnetic waves. Therefore it is reasonable to explore a region around the calculated best mixture. The hexagon design (Table 3 and Figure 3) may be used to do this. The inverse pseudocomponent transformation $x_i = L_i + R_L \cdot z_i$ can be used to map the design to the experimental region. Using a half-range of 0.15, the lower bounds on the proportions of the components would be $0.05 \leq$ powder, $0.15 \leq$ flake, and $0.35 \leq$ fiber; from the lower bounds, $R_L = .45$. The mapping for the 16-point hexagon (or uniform shell) design is given in Table 7 and illustrated in Figure 5. The design points and check points are uniformly spaced over the experimental region and therefore provide a good search for the optimum mixture without regard to the use of a polynomial model for interpolation. The design is rotatable so that if a second-order polynomial is used, the predictions will be equally precise at all points on concentric circles: only the distance from the center of the design region, and not the direction, determines the precision of the predictions (assuming the second-order polynomial model is adequate). Because of the rotatability of the hexagon design, the experimental region is usually considered to be circular (the circle in Figure 5) rather than hexagonal.

Table 7. Mapping of Uniform Shell Design

Point	z_1	z_2	z_3	x_1	x_2	x_3
1	2/3	0	1/3	.35	.15	.50
2	1/3	2/3	0	.20	.45	.35
3	0	1/3	2/3	.05	.30	.65
4	1/3	1/3	1/3	.20	.30	.50
5	1/3	1/3	1/3	.20	.30	.50
6	2/3	1/3	0	.35	.30	.35
7	0	2/3	1/3	.05	.45	.50
8	1/3	0	2/3	.20	.15	.65
9	1/3	1/3	1/3	.20	.30	.50
10	1/3	1/3	1/3	.20	.30	.50
11	5/9	2/9	2/9	.30	.25	.45
12	2/9	5/9	2/9	.15	.40	.45
13	2/9	2/9	5/9	.15	.25	.60
14	1/9	4/9	4/9	.10	.35	.55
15	4/9	1/9	4/9	.25	.20	.55
16	4/9	4/9	1/9	.25	.35	.40

$$x_1 = 0.05 + 0.45 \cdot z_1$$
$$x_2 = 0.15 + 0.45 \cdot z_2$$
$$x_3 = 0.35 + 0.45 \cdot z_3$$

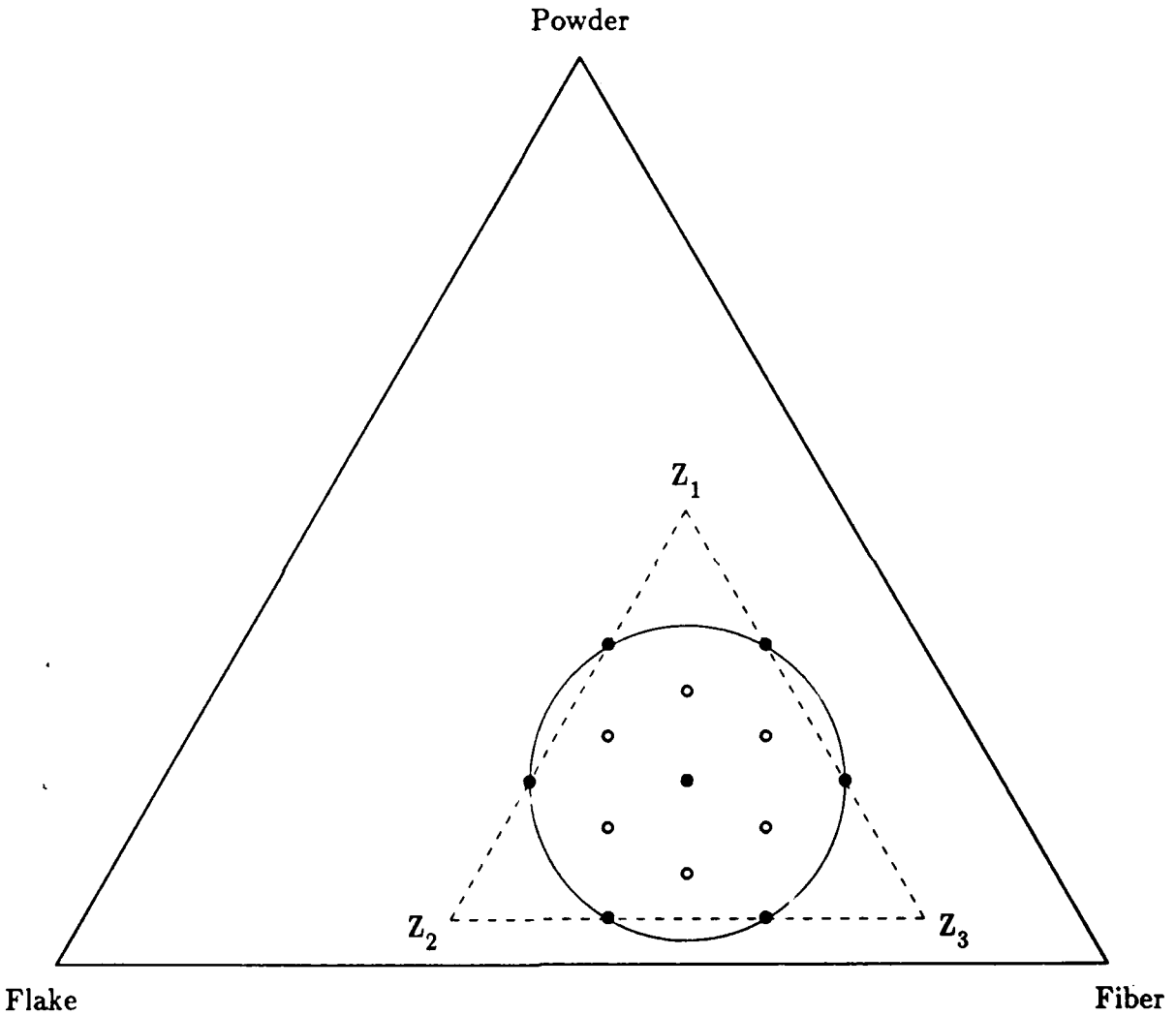

Figure 5. Application of Hexagon Design to Obscurant Smoke Formulation

7. SUMMARY

Two types of symmetry can occur when the component proportions of a mixture experiment are constrained by upper and lower bounds. Both symmetries create related points in the constrained mixture region. Sets of related points form blocks with respect to first-degree polynomial models. The presence of either type of symmetry implies that the centroid of the constrained region is uniquely defined. That is, the three methods proposed for calculation of the centroid of a mixture region yield the same result when the region is symmetric. Shortcut methods of calculating the centroid, however, depend on the type of symmetry. For regions with twin symmetry, the centroid is given by the component midranges. The centroid of a radially symmetric region can be calculated by an inverse pseudocomponent transformation of $(1/q)\mathbf{1}$.

An examination of mixture regions with both twin and radial symmetries has provided new insights into designs for mixture experiments. The uniform shell designs can be written as three-level symmetric-simplex designs for mixtures. It was shown that the 3-dimensional central composite design can be written in symmetric-simplex form for mixture experiments. The icosahedron design and the dodecahedron design were also given. A uniform shell design was applied to developing an obscurant smoke.

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APPENDIX
PROOF FOR UNIFORM SHELL DESIGNS

For the uniform shell designs, the rows of the design matrix **X** consist of shell points, given by all permutations of $(2/q, 0, 1/q, \ldots, 1/q)$, and a row for the centroid $(1/q, \ldots, 1/q)$. To show that these designs are the uniform shell designs of Doehlert,[5] transform the $N \times q$ matrix **X** to an $N \times (q-1)$ matrix **W** by

$$\left[\mathbf{0} \mid \mathbf{W}\right] = s\left[q\mathbf{X}-\mathbf{J}\right]\mathbf{P}$$

where s is a scaling factor, **J** is a matrix of all 1's, and **P** is an orthogonal matrix. By proper selection of s, **P**, and the order of the rows of **X**, **W** will be exactly the designs listed by Doehlert.[5]

The design **X** has radius $2^{1/2}/q$, so $q\mathbf{X}$ has radius $2^{1/2}$, whereas the uniform shell designs of Doehlert[5] are scaled to have radius 1. Therefore $s = 1/2^{1/2}$ is required in the equation. The orthogonal matrix **P** required for the equation can be obtained by normalizing the columns of

$$\begin{array}{ccccccccc}
1 & -1 & -1 & -1 & -1 & . & . & . \\
1 & 1 & -1 & -1 & -1 & . & . & . \\
1 & 0 & 2 & -1 & -1 & . & . & . \\
1 & 0 & 0 & 3 & -1 & . & . & . \\
1 & 0 & 0 & 0 & 4 & . & . & . \\
. & . & . & . & . & . & . & . \\
. & . & . & . & . & . & . & . \\
. & . & . & . & . & . & . & .
\end{array}$$

to have sum of squares 1. Doehlert[5] does not give all the rows of the uniform shell designs; the omitted rows can be obtained from the given rows by multiplying by -1. The row order required to obtain the designs given by Doehlert[5] from the equation above is most easily expressed as the rows of the matrix $q\mathbf{X} - \mathbf{J}$, which has elements -1, 0, and 1. The required row order is:

0	0	0	0	0	.	.
−1	1	0	0	0	.	.
−1	0	1	0	0	.	.
0	−1	1	0	0	.	.
−1	0	0	1	0	.	.
0	−1	0	1	0	.	.
0	0	−1	1	0	.	.
−1	0	0	0	1	.	.
0	−1	0	0	1	.	.
0	0	−1	0	1	.	.
0	0	0	−1	1	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.

Other choices for s and $\mathbf{P}$ in the above equation give the uniform shell designs in a different orientation or with a different scaling (or both). Some of the other orientations are much better than the orientation used by Doehlert,[5] which gives the first variable 5 levels, the last variable 3 levels, and all other variables 7 levels. For $q = 4$, 8, 12, and 16, the use of $s = 1/2$ and a Hadamard matrix (not scaled to be an orthogonal matrix) for $\mathbf{P}$ in the equation above gives the uniform shell designs for 3, 7, 11, and 15 variables as 3-level designs with levels -1, 0, and 1. The 3-variable design is the same design as the Box-Behnken[17] design, but the designs for 7, 11, and 15 variables are new designs. The uniform shell designs for other numbers of variables can usually be rotated to have mostly 5-level factors with one 3-level factor and sometimes one 7-level factor.